

# The Effect of Shortening Stability on Commercially Produced Army Ration Biscuits. II. Development of Oxidation During Storage\*

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AN experiment involving the commercial production and packaging of two types of Army ration biscuits prepared from common ingredients with nine lots of vegetable oil shortenings of increasing stability values and two lots of lard as the only ingredient variables was reported in a preceding paper (2). Also presented therein were the results of accelerated tests on the 11 lots of shortenings and the 22 lots of biscuits. The present paper will discuss the significance of those results in terms of actual storage tests on the biscuits under three different conditions of packaging and two different storage temperatures.

## Experimental

Since each scheduled examination during the two-year period involved 132 individual samples, presentation of complete data was considered inadvisable.<sup>3</sup>

The factors considered significant in the development of oxidation in the biscuits are discussed under each type of packaging employed. The codes are the same as used in the preceding paper (2). Code 1L consists of prime steam lard; code 2L, the same lard plus 0.02% nordihydroguaiaretic acid; code C, a series of 6 hydrogenated cottonseed oil shortenings; and Code S, a series of 3 hydrogenated soybean oil shortenings. The A.O.M. values for the corresponding shortening codes are contained in the second column of Table I.

**Biscuits Stored in Cartons.** Biscuits stored in cartons at 100°F. were examined organoleptically for rancidity by two experienced observers. Although after one month of storage several of the lots were found to be rancid, it became apparent that the shortening in the biscuits was not responsible. Zero peroxide values on the shortening extracted from the biscuits indicated little or no change due to oxidation. Rancimeter values on two of the lots considered rancid were identical with their respective original values. Consumer acceptance tests rated all of the biscuits acceptable (1). For several successive examination periods the rancid odors and flavors became more objectionable, but consumer acceptance tests still failed to support these findings. In a few of the lots containing the least stable shortening measurable peroxides developed prior to the second-month examination. On additional storage they continued to increase in a normal manner. Typical data obtained on the Type I and Type IV biscuits containing cotton-

seed oil shortening are presented in Fig. 1. Further investigation revealed that the "initial rancidity" disappeared after a few days, thus accounting for differences in opinions of the two observers and those registered by the taste panel. The latter did not score the biscuits until several days after the cartons had been opened.

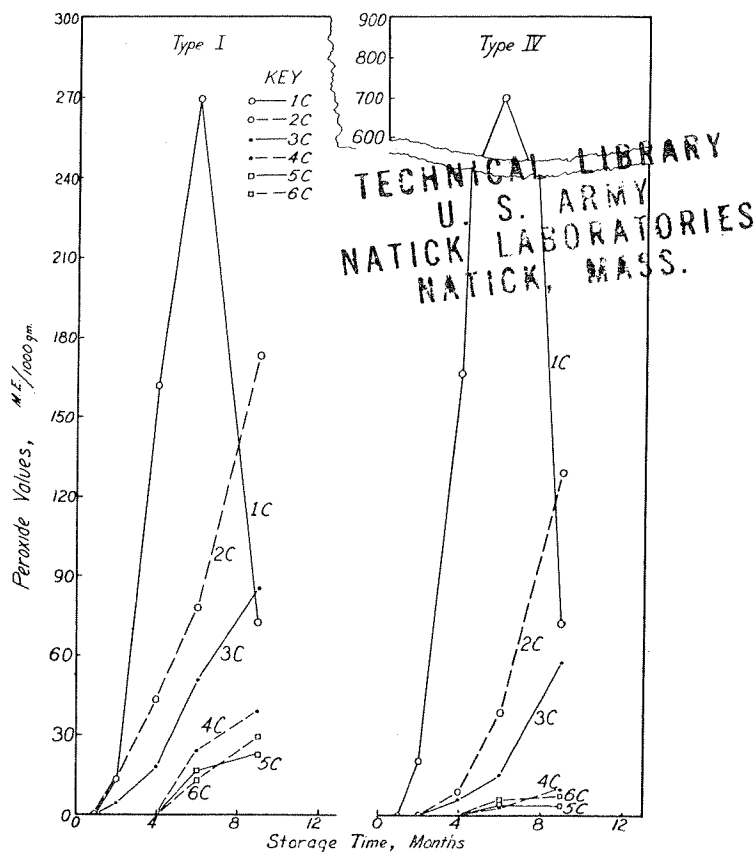


FIG. 1. Rate of peroxide formation in biscuits stored in cartons at 100°F.

It was observed at the first examination period that the inside corners of some of the cartons were slightly oil-soaked, the spread becoming more pronounced at each subsequent examination. The rancid volatile odors, which were detected when the cartons were opened, probably came from these oil-soaked areas of the carton, and it was presumed that these odors were transferred by diffusion to the biscuits.

To determine the chemical condition of the shortening absorbed in the carton material, six random lots of Type IV biscuits were selected for further investigation. The cartons were cut into small pieces, ten grams of both the oil-soaked and non-oil-soaked were extracted at room temperature with 50 ml. of chloroform, and peroxide values were determined on a 20-ml. aliquot of the filtered solutions in the same manner as was previously described for the biscuits

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<sup>3</sup> Complete data on moisture, pH, and Kreis test were obtained at each scheduled examination but, since they were too voluminous to present within the limits of this paper, they were not presented in detail but are summarized as follows:

1. The moisture content of each lot of biscuits was uncontrolled and slight variations were observed throughout the entire study. Only one trend was noticed: biscuits stored in cartons and punched cans slowly lost moisture on storage on account of the low relative humidity of the storage rooms.

2. A slight decrease in pH occurred with time, becoming more marked as rancidity developed.

3. The Kreis test results (semi-quantitative) tended to substantiate the peroxide values.

(2). The peroxide value of the fat absorbed in the carton material was calculated as follows:

$$P.V. = \frac{(V_s - V_b) \times N \times 1000}{(W_s - W_b) \times 4}$$

where

P.V. = peroxide value in terms of milliequivalents/1000 grams of fat.

$V_s$  = ml. of  $\text{Na}_2\text{S}_2\text{O}_3$  required to titrate a 20-ml. aliquot of the extract from the oil-soaked carton.

$V_b$  = ml. of  $\text{Na}_2\text{S}_2\text{O}_3$  required to titrate a 20-ml. aliquot of the extract from the non-oil-soaked carton.

$N$  = normality of  $\text{Na}_2\text{S}_2\text{O}_3$ .

$W_s$  = grams of soluble material in 5-ml. aliquot of extract from oil-soaked carton.

$W_b$  = grams of soluble material in 5-ml. aliquot of extract from non-oil-soaked carton.

Fig. 2 shows the changes in peroxide values which occurred in the fat absorbed in the carton material. It can readily be observed that these values decreased with storage time. Considering a typical oxidation curve (Fig. 1, Lot 1C), it is apparent that these

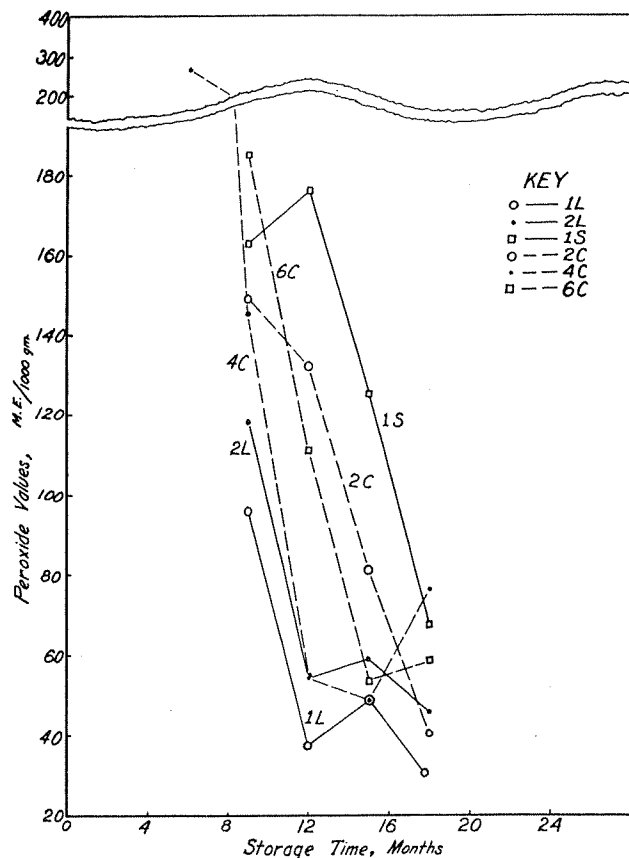


FIG. 2. Change in peroxide values of fat extracted from carton material stored at 100°F. (Type IV biscuits.)

peroxide values are receding from a maximum and that the shortenings absorbed in the cartons were in a rancid condition prior to the sixth-month examination. Beyond reasonable doubt the absorbed fat was the source of the volatile rancid odors. Both types of biscuits in cartons at 70°F. also developed "initial rancidity" prior to the second month of storage.

Differences in rate of oxidation of the fat remaining in the biscuits and that absorbed in the carton may be explained as the combined effect of increased surface area and of metal catalysis. The carton material contained large amounts of copper (10 to 88 p.p.m.) and iron (80 to 780 p.p.m.) distributed in a heterogeneous manner.

*Biscuits Stored in Cans.* Storage data obtained on biscuits held at 70° and 100°F. in both punched and sealed cans are summarized in Table I. Initial

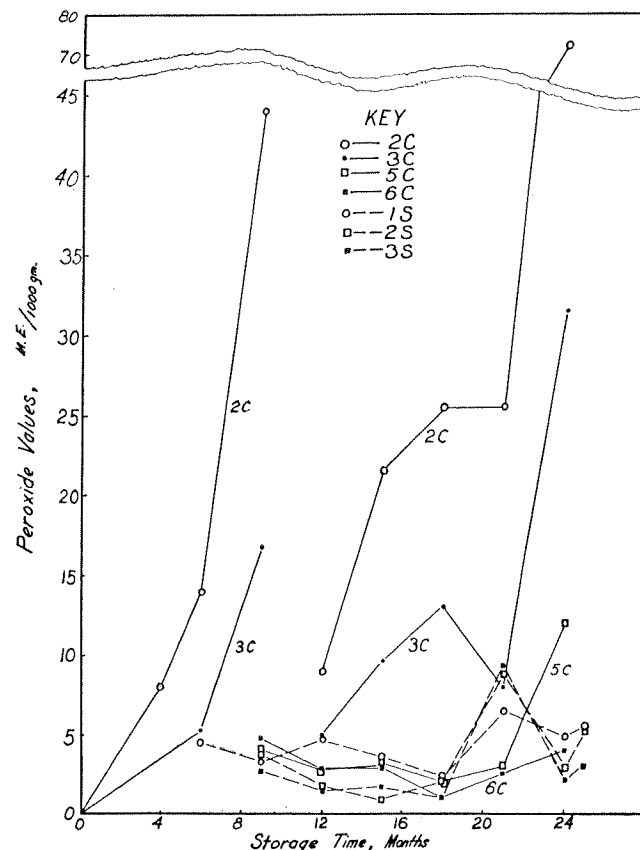


FIG. 3. Rate of peroxide formation in Type I biscuits stored in punched cans at 70°F.

A.O.M. values and Rancimeter values previously reported (2) are included in the table for comparative purposes. Organoleptically, storage life was determined by the two previously mentioned observers who considered only the development of typical rancidity. Chemically, storage life was determined from peroxide value curves. The peroxide value corresponding to the development of rancidity in the biscuits containing the hydrogenated cottonseed and soybean oil shortening stored in punched cans at 100°F. was observed to be between 130 and 190 milliequivalents per kilogram of fat. For the purposes of this study 150 m.e. was selected as the value which most nearly corresponded to the development of organoleptic rancidity. A peroxide value of 20 m.e. appeared to correspond to development of rancidity in the biscuits containing lard.

Since examinations were made at 1, 2, 4, 6, 9, 12, 15, 18, 21, and 24 months, the development of rancidity is shown as occurring between two of these periods. The maximum value indicates definite rancidity while the minimum value indicates the absence

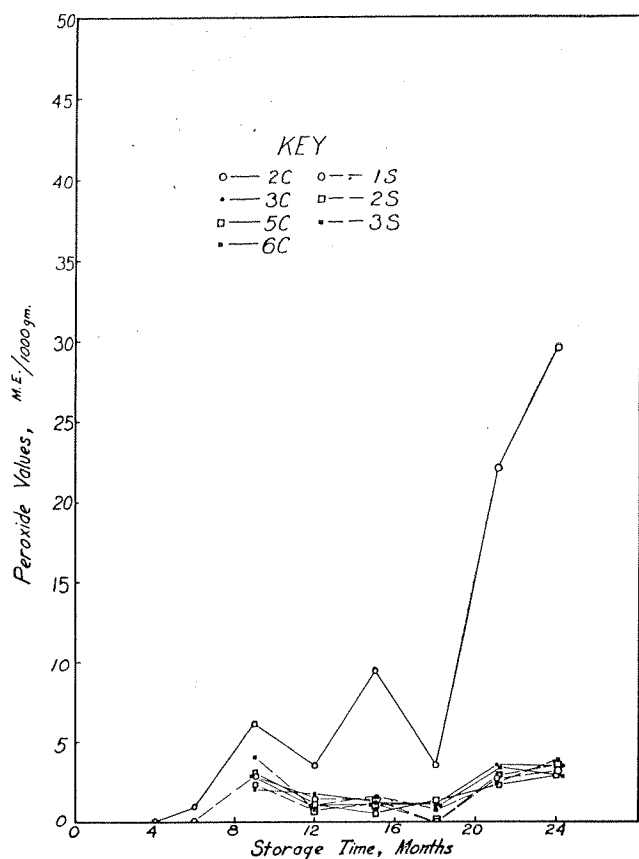


FIG. 4. Rate of peroxide formation in Type IV biscuits stored in punched cans at 70°F.

of rancidity for their respective examination periods. In a few cases it was impossible to establish the development of rancidity in biscuits stored in sealed cans between two immediately succeeding periods. All

cases in which chemically and organoleptically determined rancidity did not occur during the two-year storage period are indicated as greater than 24 months. Both Table I and the peroxide value curves referred to in the table will be the basis for all following discussion.

**Biscuits Stored in Punched Cans.** The development of peroxides in Type I and Type IV biscuits stored at 70°F. is shown in Figs. 3 and 4. Curves not plotted fit the general pattern as would be anticipated on the basis of the results of the accelerated tests.

Two separate curves are shown in Fig. 3 for each of Lots 2C and 3C since the original samples held at 70°F. became weevil-infested and were discarded after the ninth month. For the twelfth month and all subsequent examinations data were obtained on an identical series of samples which were being held at the same temperature but at a higher relative humidity. The curves for the first nine months were established on samples which had been held at 45% relative humidity (uncontrolled, but quite constant) while the curves after the ninth-month examination were obtained on samples which had been held at a relative humidity ranging from 50 to 70%. The biscuits held at the lower relative humidity decreased in moisture content from approximately 5.5 to 4% while those held at the higher relative humidity increased in moisture content to approximately 7%. These results are in line with the data reported by Marshall *et al.* (3) who found that increasing the moisture content of ration type biscuits decreased the rate of oxidation.

Figs. 5 and 6 show the rate of peroxide formation in Type I and Type IV biscuits stored at 100°F. Data on Lots 1C, 4C, 1L, and 2L are not presented in graphic form. Eleven of the 22 lots of biscuits became rancid during the two-year test under this condition of storage.

TABLE I  
Storage Data on Biscuits in Punched and Sealed Cans

Shortening		Biscuits											
		Rancimeter Value (2) (Initial)	Type I				Reference to P. V. Curves (Fig. Nos.)	Rancimeter Value (2) (Initial)	Type IV				Reference to P. V. Curves (Fig. Nos.)
			Storage Life						Storage Life				
			Months at 70°F.		Months at 100°F.				Months at 70°F.		Months at 100°F.		
Lot No.	Initial A.O.M. Value (2), Hours		Chemical <sup>1</sup>	Organo-leptic <sup>2</sup>	Chemical <sup>1</sup>	Organo-leptic <sup>2</sup>			Chemical <sup>1</sup>	Organo-leptic <sup>3</sup>	Chemical <sup>1</sup>	Organo-leptic <sup>3</sup>	
Punched Cans													
1L.....	5	16.5	>24	>24	6.5	6-9		15.5	>24	>24	4.0	2-4	
2L.....	21	22.0	>24	>24	7.0	6-9		19.0	>24	>24	6.0	4-6	
1C.....	22	14.0	18	18-21	3.5	4-6		14.0	14.5	18-21	4.0	4-6	
2C.....	40	25.5	>24	>24	8.5	9-12	3, 5	27.5	>24	>24	10.0	12-15	4, 6
3C.....	78	29.5	>24	>24	21.0	18-21	3, 5	55.0	>24	>24	>24	>24	4, 6
4C.....	143	51.0	>24	>24	>24	>24		72.0	>24	>24	>24	>24	
5C.....	176	53.0	>24	>24	>24	>24	3, 5	78.5	>24	>24	>24	>24	4, 6
6C.....	264	62.0	>24	>24	>24	>24	3, 5	82.5	>24	>24	>24	>24	4, 6
1S.....	59	35.5	>24	>24	>24	21-24	3, 5	35.5	>24	>24	24.0	24	4, 6
2S.....	175	81.0	>24	>24	>24	>24	3, 5	82.5	>24	>24	>24	>24	4, 6
3S.....	283	106.0	>24	>24	>24	>24	3, 5	106.0	>24	>24	>24	>24	4, 6
Sealed Cans													
1L.....	5	16.5	21	>24	....*	4-6	8	15.5	>24	9-18*	....*	2-4	
2L.....	21	22.0	23	>24	....*	9-12	8	19.0	>24	9-18*	....*	4-18*	
1C.....	22	14.0	10	12-15	....*	6-9	7, 10	14.0	....*	12-15	....*	6-15*	9
2C.....	40	25.5	24	>24	....*	6-9	7, 10	27.5	>24	>24	....*	18-21	9
3C.....	78	29.5	>24	>24	....*	15-18		55.0	>24	>24	....*	15-18	9
4C.....	143	51.0	>24	>24	....*	18-21	7, 10	72.0	>24	>24	....*	15-18	9
5C.....	176	53.0	>24	>24	....*	21-24		78.5	>24	>24	....*	18-24*	9
6C.....	264	62.0	>24	>24	....*	>24	7, 10	82.5	>24	>24	....*	18-24*	9
1S.....	59	35.5	>24	>24	....*	21-24	8	35.5	>24	>24	....*	15-18	
2S.....	175	81.0	>24	>24	....*	>24	8	82.5	>24	>24	....*	>24	
3S.....	283	106.0	>24	>24	....*	>24	8	106.0	>24	>24	....*	>24	

<sup>1</sup> Based on P.V. of 20 m.e. for lard and 150 m.e. for vegetable shortening. <sup>2</sup> Evaluated by 2 observers for rancidity only. \* Erratic.

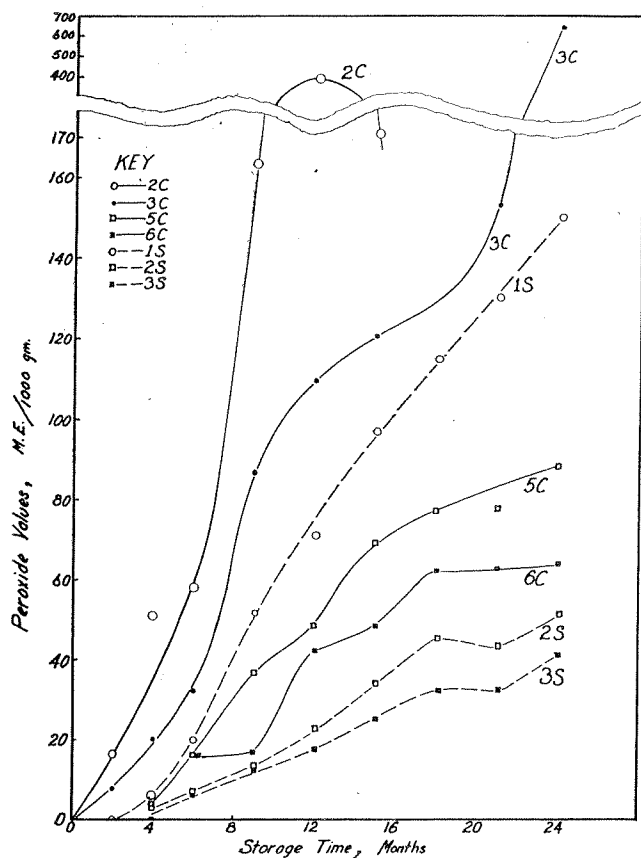


FIG. 5. Rate of peroxide formation in Type I biscuits stored in punched cans at 100°F.

*Biscuits Stored in Sealed Cans.* Typical rates of peroxide formation for biscuits stored at 70°F. are shown in Figs. 7, 8, and 9. It should be observed that the scales used in plotting the peroxide values are not identical for these figures. Pertinent data not plotted are included in Table I. Only four lots of the biscuits stored at 70°F. were considered rancid after 24 months of storage.

Peroxide curves obtained from biscuits stored in sealed cans at 100°F. were erratic. Although not presented, the curves for the Type IV biscuits were extremely erratic, making it impossible to establish any trends whatsoever. For the same reason it was not possible to establish trends in the organoleptically determined storage life shown in Table I. Peroxide curves for four lots of Type I biscuits stored at 100°F. are presented in Fig. 10. Although the curves are erratic, the peroxide values appear to increase to a maximum and then decrease. At the maximum value obtained or at the next following examination period, rancidity was quite pronounced as would be expected when oxidation products rapidly break down. Type IV biscuits stored in sealed cans at 100°F. developed only small amounts of peroxides prior to the development of rancidity as organoleptically determined—which would indicate that perhaps commercial lecithin accelerated the breakdown of the peroxides or influenced the formation of less stable peroxides under the conditions of this phase of the experiment.

#### Discussion and Conclusion

When the ration biscuits were stored in cartons at both 70° and 100°F., rancidity was organoleptically

detected in the biscuits prior to the second-month examination. These rancid odors and flavors were derived from absorbed fat in the fiberboard cartons and did not originate in the biscuits. Rapid oxidation, probably accelerated by excessive amounts of copper and iron, produced rancidity in the absorbed fat and the rancid odors diffused into the biscuits. The generally poor acceptability of ration biscuits during World War II may be ascribed to the type of container used for overseas shipment.

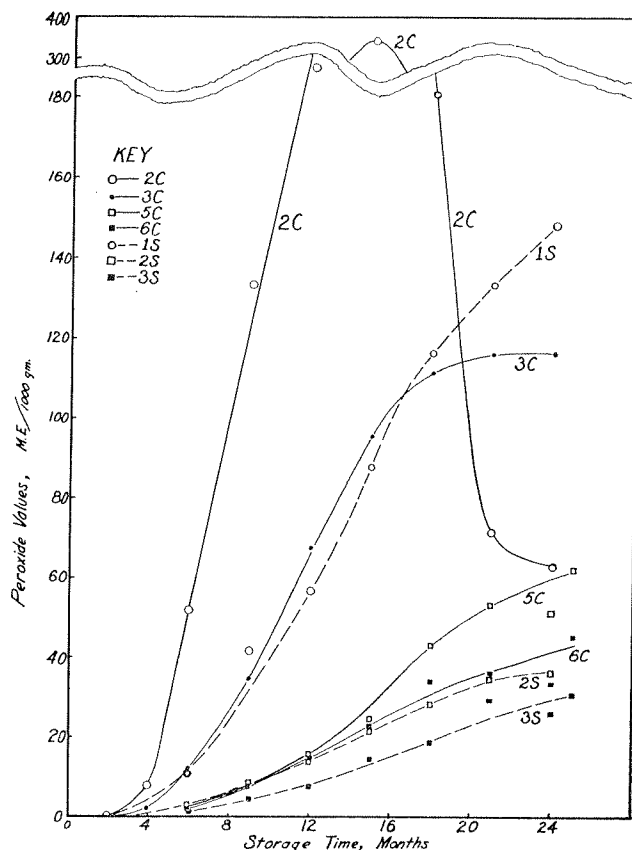


FIG. 6. Rate of peroxide formation in Type IV biscuits stored in punched cans at 100°F.

The present shortening specification for ration biscuits requires a minimum A.O.M. value of 100 hours. It can be observed (Table I) that this value lies between the A.O.M. values obtained on shortening Lots 3C and 4C. Considering only the development of rancidity, this specification appears to be adequate protection up to 12 months of storage at a maximum temperature of 100°F. for either the Type I or Type IV biscuit stored in sealed cans or adequate breather-type containers.

Differences in the storage life of the Type I and Type IV biscuits containing cottonseed oil shortening, stored in punched (breather type) cans and in sealed cans, were of particular interest. Apparently, the adding of commercial lecithin to Type IV biscuits retarded the development of peroxides in these biscuits. However, in the sealed cans rancidity was detected at lower peroxide values, offsetting the effect of lecithin which appeared to decrease the rate of oxidation at the level used. Differences in the storage life of the two types of biscuits stored in sealed cans

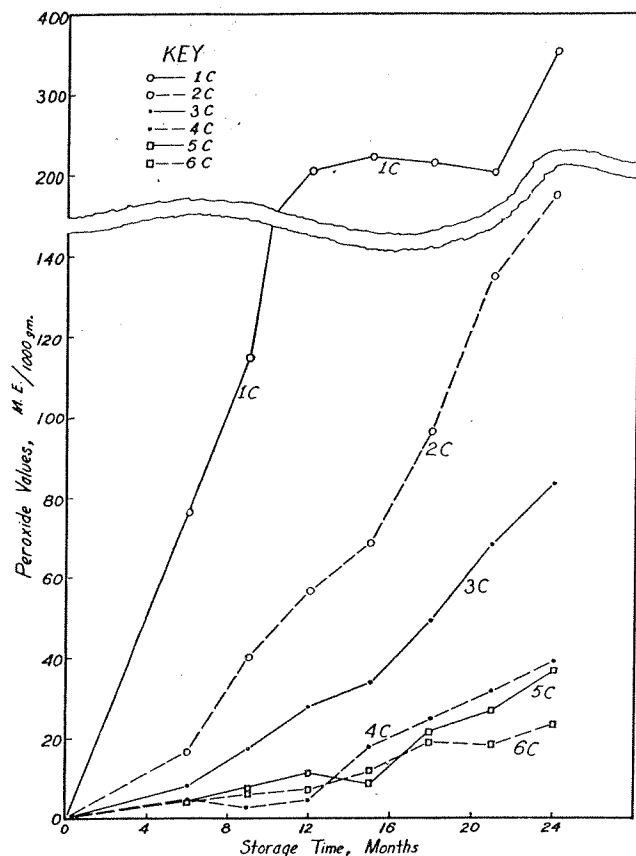


FIG. 7. Rate of peroxide formation in Type I biscuits stored in sealed cans at 70°F. (Cottonseed oil shortening.)

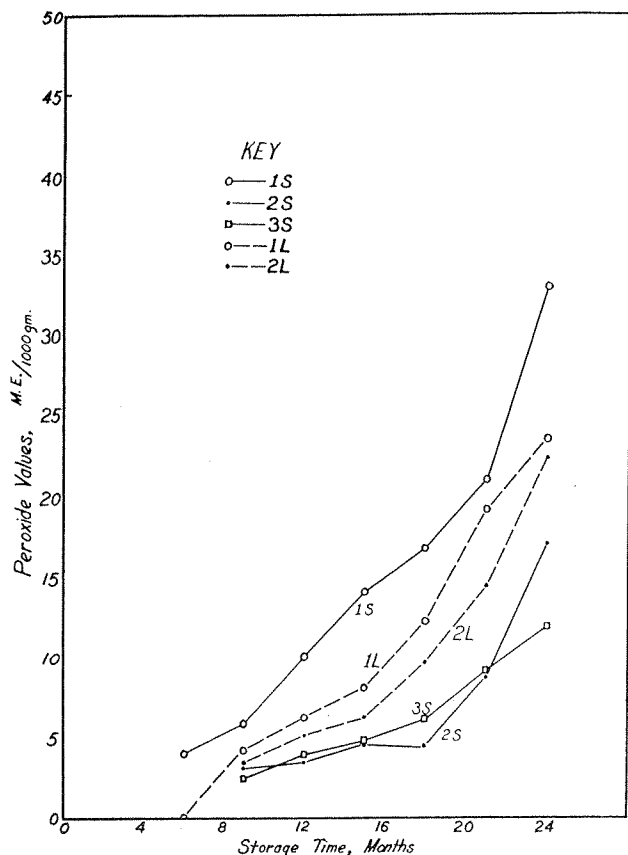


FIG. 8. Rate of peroxide formation in Type I biscuits stored in sealed cans at 70°F. (Soybean oil shortening and lard.)

were not observed. In punched cans the storage life of Type IV biscuits containing cottonseed shortening was greater than that of Type I biscuits.

Biscuits prepared with lard plus nordihydroguaiaretic acid (2L) were more stable than those containing lard alone (1L); however, insofar as Army ration biscuits are concerned, the increased stability obtained by the addition of this antioxidant to lard was not of great significance. The Type IV biscuits containing lard and lard plus nordihydroguaiaretic acid developed rancidity earlier than did the corresponding Type I biscuits, probably due to the addition of the lecithin to the Type IV biscuits.

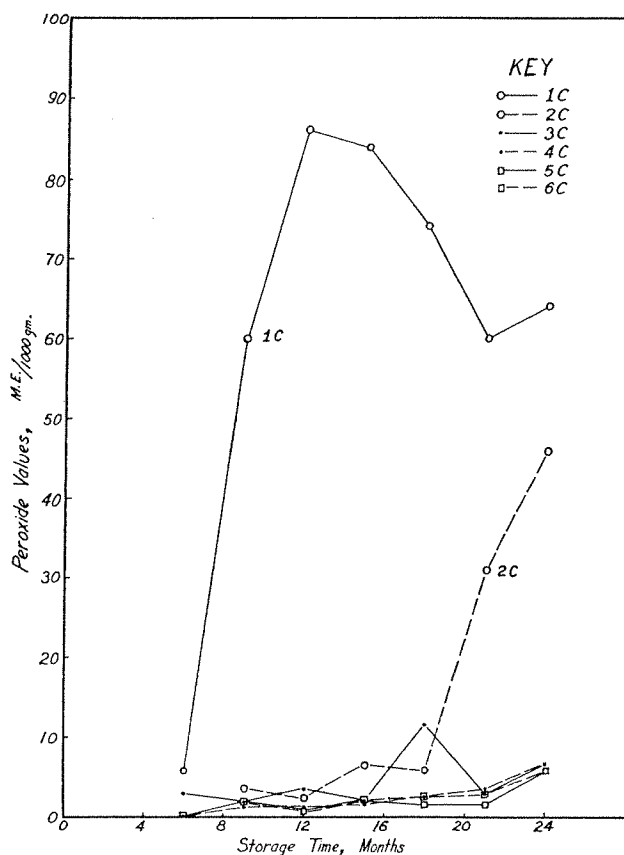


FIG. 9. Rate of peroxide formation in Type IV biscuits stored in sealed cans at 70°F.

Considering the data presented, it is practically impossible to expect any accelerated test to correlate with storage tests under the numerous conditions of storage which might be encountered. Although accelerated tests can be fairly well controlled, variables such as moisture content, trace metal contamination, the effect of packaging in different types of containers, available oxygen to fat ratio, etc., affect the actual life of the product. However, these accelerated tests are of value for comparative purposes, even though their results must be interpreted with care.

The data obtained by the accelerated Rancimeter test corroborate to a great extent actual storage results obtained on the biscuits stored in punched cans. From the Rancimeter data presented in the first paper (2) differences in the storage life of the two types of biscuits were indicated. These data in general were substantiated by the rate of peroxide formation in the biscuits stored in punched cans (Figs. 3, 4, 5,

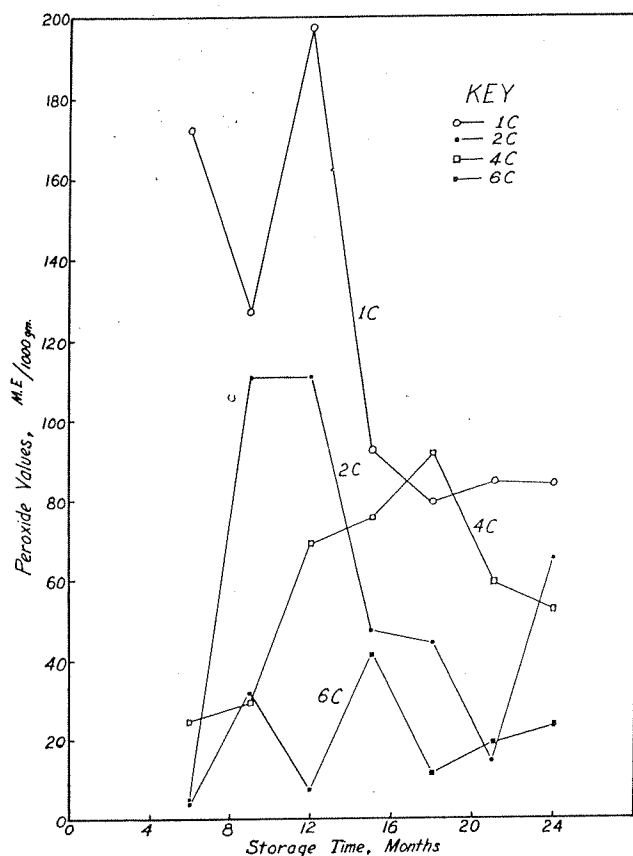


FIG. 10. Rate of peroxide formation in Type I biscuits stored in sealed cans at 100°F.

and 6). Where storage conditions require a hermetically sealed container, the use of the Rancimeter method for ration biscuits would appear to be of questionable value in estimating relative shelf life.

### Summary

The comparative rates of oxidation of the shortening in 22 lots of biscuits held under three different conditions of packaging at two different storage temperatures have been discussed. Relating stability tests to storage tests is practically impossible considering the numerous conditions of storage which might be encountered. Accelerated tests, however, are valuable for comparative purposes.

Considering only the development of "rancidity," a 100-hour shortening appears to be adequate protection up to 12 months of storage at a maximum temperature of 100°F. for either Type I or Type IV Army ration biscuits when stored in either sealed cans or adequate breather-type containers.

The poor storage life of Army ration biscuits, packaged in fiberboard containers, was shown to be due primarily to the nature of the packaging material.

Insofar as Army ration biscuits are concerned, the addition of N.D.G.A. to lard does not result in a significant increase in biscuit stability.

### REFERENCES

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3. Marshall, J. B., Grant, G. A., and White, W. H., Can. J. Res., Sect. F, 23, 286-292 (1945).